

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE
ELECTROLYTIC ALUMINISING OF SHAPED METAL
ARTICLES

(71) We, SIEMENS AKTIEN-
GESELLSCHAFT, a German Company of
Berlin and Munich, Germany, do hereby
declare the invention, for which we pray that
5 a patent may be granted to us, and the method
by which it is to be performed, to be partic-
ularly described in and by the following state-
ment:—

This invention relates to a process for
10 electrolytically aluminising shaped articles
made of light metals and alloys.

Owing to the chemical and material proper-
ties of such light metals as beryllium, mag-
nesium, zinc, aluminium and titanium and
15 alloys of which these metals form the major
component, the surface properties of shaped
articles formed therefrom cannot be modified
sufficiently for practical requirements, and the
20 articles cannot be provided with metal coatings
of satisfactory quality in aqueous or protic
media.

It is frequently desired to coat or surface
25 modify shaped articles made of beryllium,
magnesium, zinc, aluminium and titanium or
alloys of which these metals form a major
part because of the material and surface pro-
perties of such metals. However, since these
30 are without exception relatively base metals,
their surfaces fairly quickly form a substan-
tially oxidic surface layer when exposed to the
atmosphere. This layer generally protects the
metal therebeneath from further corrosive
attack.

Attempts have already been made to remove
35 this surface layer by sand-blasting. However,
an oxide layer is immediately formed by the
ambient air owing to the affinity for oxygen
of this relatively base material, and this oxide
layer makes difficult or even prevents subse-
40 quent electrodeposition of a metal coating.
This is a serious disadvantage since the use of
these materials, particularly in air and space
travel, automobile and vehicle construction, is
becoming of ever increasing importance
45 because of their low specific gravity.

The extent to which the aforesaid shaped

articles undergo atmospheric corrosion protec-
tion is very greatly dependent on the degree of
purity of the metal and, with alloys, on the
nature of the alloy components. In general,
the corrosion rate decreases with an increasing
degree of purity of the metal. In practice, the
constituents of alloys cannot be chosen solely
in accordance with their favourable influence
on the corrosion behaviour of the main metal
of the alloy, and are generally selected to im-
prove the mechanical and commercial proces-
sing or casting properties of the main metal.
Thus, iron obtained in extremely pure form
by drawing in stages and melting in suspen-
sion is hardly affected by rust in moist air;
electron metal, which is an alloy with 90%
or more of magnesium and, depending on the
purpose of use, additions of Al, Zn, Mn, Cu
and silicon, can be very easily machined, but
undergoes rapid atmospheric corrosion.
Aluminium pressure casting alloys which have
considerable commercial importance, for ex-
ample DGAISi10(Cu), DGAISi12 and
DGSi6Cu3, cannot be coated by anodising or
can only be coated with oxide of an unsatis-
factory quality and then have a displeasing grey
colour tone.

Beryllium and beryllium alloys, which are
desirable modern materials because of their out-
standing strength coupled with very low speci-
fic gravity (1.86), lack a dense, firmly adher-
ing and non-toxic surface protective film,
which protects them from relatively strong
attack by corrosion.

Titanium and titanium alloys, because of
their excellent mechanical properties coupled
with a relatively low specific gravity (4.51),
are being used to an increasingly greater ex-
tent in air and space travel and also in machine
construction and the chemical industry. The
thin oxide film (rutile) which is quickly formed
gives them an excellent protection against cor-
rosion in oxidising media. It is true that this
oxide film can be intensified by anodic oxida-
tion. However, this coating differs from the
anodic oxidation coating which can be ob-

[Price 25p]

tained with aluminium in having a deep violet-blue to bluish-red colouring and not having the honeycomb structure which is peculiar to aluminium and which makes possible the excellent suitability for colouring of the colourless anodic coating of aluminium and the consolidation or sealing thereof. The titanium materials also do not possess the bright colour tone of aluminium and its good electrical conductivity.

Zinc and zinc alloys also develop oxidic protective surface coatings as a result of atmospheric oxidation. These coatings protect the metal therebeneath from extensive corrosion.

Unlike with aluminium, however, no processes have so far been described for strengthening this protective layer on zinc materials by anodic oxidation to build up oxide coatings, the structure of which permits the incorporation of dyestuffs.

The very rapid development of oxidic or hydroxidic surface layers in air or in aqueous pretreatment and electrolyte media is very detrimental to the electrodeposition of metal coatings and surface improvement of the aforesaid light metal materials in aqueous or protic electrolyte baths. The surface layers which are always present in aqueous media prevent or largely impede the direct electrocoating of the specimen and impair the electrocrystallisation and reduce the bonding strength and homogeneity of the coating metal formed. The electrocoating of light metal articles, more especially beryllium and magnesium materials, from aqueous electrolyte media is consequently a considerable problem.

According to the present invention, there is provided a process for applying an aluminium coating to a shaped article formed from a metal which is attacked by aqueous or protic media or by oxygen to form an oxidic or hydroxidic or salt surface coating, which comprises providing the shaped article with surface(s) free from said coating in the presence of an anhydrous aprotic liquid which is inert to the metal and which covers the surface(s) of the shaped article to be aluminised, and, without exposing said surface(s) to an aqueous or protic medium or to oxygen, electrolytically depositing aluminium on the said surface(s) from an oxygen-free and water-free aprotic organo-aluminium electrolyte. Although the process is generally applicable to any metal which forms oxidic and hydroxidic or salt coatings in the atmosphere or in aqueous media respectively, the process is expected to find particular use with articles formed of the low density metals beryllium, magnesium, zinc, aluminium and titanium and alloys comprising a said metal which constitutes, or a plurality of said metals which, taken together constitute, the major component of the alloy. Examples of other metals to which the process can be applied are zirconium, niobium, tantalum and tungsten.

By providing the surfaces to be coated with aluminium covered with an aprotic medium, such as an organometallic electrolyte medium, it is possible to obtain metal surfaces which are bright and free from surface coatings. These coatings do not show signs of corrosion and thus make possible a perfect and direct deposition of aluminium on to the light metal surface.

The surfaces will generally be produced by pretreating the shaped articles in the presence of an anhydrous aprotic liquid to remove surface coatings of the above-described type. The pretreatment can if necessary take place with the exclusion of air in an inert gas atmosphere. Such an atmosphere should be present if the articles are to be cleaned to yield a bright surface before effecting electrodeposition of aluminium thereon. The shaped articles otherwise react in aqueous or protic media and in air and develop oxidic or hydroxidic or salt surface coatings, which prevent or at least impede the electrodeposition of aluminium and reduce or impair the bonding strength of this protective metal.

In accordance with one embodiment of the invention, the pretreatment is carried out by pressure blasting with particles of hard substance suspended in inert aprotic anhydrous liquids, which are insufficiently volatile to vapourise under the pressure blasting conditions and expose to the ambient atmosphere the surface(s) undergoing pressure blasting. Such liquids include oils, for example paraffin oils and silicone oils, and certain optionally halogenated, preferably chlorinated, hydrocarbons, in particular carbon perhalides. A preferred pressure blasting agent is corundum powder dispersed in thinly liquid oils. Blasting pressures of from 1 to 10 atm gauge, advantageously 3 to 7 atm gauge, will generally be used. The particle sizes of the hard substance will be in the range of from 50 to 200 μm . The suspending medium can be circulated by pumping or accelerated with compressed air or inert gas (nitrogen) to serve as driving medium.

The hydrophobic, air-repelling and moisture-repelling liquid film surrounding the particles of hard material displaces air and moisture as it makes impact with the metal surface to be cleaned, so that the particles of hard material inside the liquid film break through the oxidic surface coating and expose the bright metal surface, which is protected against access of air and moisture by the liquid film.

The pretreatment in the aforesaid manner is thus a preserving mechanical treatment of the surface of the shaped article. The extent of erosion of the surface is in the range of from only a few tenths to a few μm of surface thickness. Thicker layers of oxide and scale can be removed beforehand by sand-blasting or chemical pretreatment in conventional manner. With freshly manufactured greased workpieces,

however, this is unnecessary. The oxide layers which form at room temperature on a dry surface can be removed immediately by pressure blasting with particles of hard material suspended in oil. Thus greased workpieces can be subjected, as such, to the surface pretreatment of the process according to the invention without the need to effect degreasing.

The surface pretreatment process using pressure blasting in oil, which can be used in practice on all greased materials, comprises the following treatment steps:

- 15 Treatment step 1, mechanical fabrication of the workpiece,
- 15 " " 2, the oily or greased workpiece is blasted under pressure,
- 20 " " 3, the particle-containing oil film is detached by dipping in liquid perchloroethylene, and
- 25 " " 4, the grease is completely removed by perchloroethylene vapour degreasing,
- 30 " " 5, while retaining a film of condensed perchloroethylene thereof, the workpiece is immediately immersed in toluene and rinsed therein, possibly with ultrasonic action,
- 35 " " 6, it is immediately lowered into the aluminising bath, while retaining a surface film of the toluene, for coating with electro deposited aluminium, without cleaning off the toluene.

By varying the nature and size of the particles of hard material, the viscosity of the oil and blasting pressure, it is possible to provide suitable working conditions for each material and each surface quality, and to obtain bright metal surfaces which are free from a covering coating.

It is to be noted that this procedure for the surface pretreatment operates with a few treatment steps and without any aqueous etching and rinsing baths and thus no problems arise in connection with disposal of waste waters.

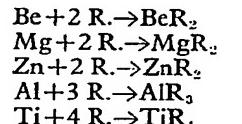
The surface pretreatment step of the process according to the invention can also be effected by liquid drop bombardment erosion with inert, non-aqueous aprotic liquids. Such a process is described, for example, in German Auslegeschrift No. 1,614,690. This form of the surface pretreatment is particularly suitable for use with material in strip or sheet form when employing a continuous working method, and is the best procedure to adopt

with such material. This pretreatment procedure is characterised by the following steps:

- 65 Treatment step 1, production of the sheet material and feeding the strip material from the drum,
- 70 " " 2, oily or greased sheet material is subjected to liquid drop bombardment erosion with, for example, benzene or toluene, if necessary after it has been heated,
- 75 " " 3, the cleaned and bright material still wetted with benzene or toluene enters the aluminising cell.

For safety reasons, the liquid drop bombardment erosion is generally carried out under a nitrogen atmosphere or with carbon perhalides. It is again possible to obtain bright metal surfaces free from a covering coating.

Another surface pretreatment procedure which can be used is the anodic detachment of a thin surface layer of the metal shaped article in an oxygen-free and water-free aprotic organometallic electrolyte medium, especially an organoaluminium electrolyte. Preferred electrolytes are those containing triethyl aluminium and trimethyl aluminium. The ethyl and methyl radicals, respectively, which are formed anodically with the passage of current react with the light metals to form liquid metal alkyls (MR_n), as for example,

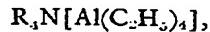


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While beryllium and aluminium can also be anodically decomposed in an aluminising electrolyte media which contains halide, and more especially fluoride, this is not possible with the magnesium and zinc materials, because of the formation of insulating MgF_2 and ZnF_2 surface layers, respectively. The most suitable aluminising electrolytic media for all light metal articles are the tetraalkyl alanate complexes (alanates are derivatives of alanes which are derivatives of aluminium hydride, AlH_3 , in a manner analogous to silanes being derivatives of silane, SiH_4), which are free from halide ions, for example:



and



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wherein R is an alkyl radical, the Na-K

mixed salt of tetraethyl alanate melting at 70°C being particularly advantageous. Na[Al(C₂H₅)₄] alone only melts at 128°C.

- 5 The metal articles which are anodically loaded in these melt electrolytes and are thereby surface pretreated can be lowered while still moist with electrolyte and under an inert gas atmosphere into the aluminising cells and can be coated by cathodic loading with electrodeposited aluminium.

In the case of shaped articles of beryllium and aluminium, such anodic surface pretreatment can take place directly in the aluminising cell and the bright or bare metal surface can have aluminium electrodeposited thereon by reversal of polarity; this particularly advantageous form of surface pretreatment in an aprotic electrolyte medium which is free from oxygen and water involves the following sequence of operation:

- Treatment step 1, perchloroethylene vapour degreasing and removal of water from the surface of the workpiece,
 25 " " 2, washing in toluene, possibly with ultrasonic action,
 " " 3, toluene-moist workpiece is lowered in the aluminising bath and anodically loaded for a short time (about 15 minutes) with electrode movement for detaching surface film,
 30 " " 4, polarity reversed and electrodeposition of aluminium.

In the case of shaped articles made of magnesium, zinc and titanium, the initial procedure is likewise in accordance with the treatment steps 1 and 2. Then the article moist for example with toluene is lowered into the pretreatment melt electrolyte bath, for example, a 1:1 mixture of Na[Al(C₂H₅)₄] and K[Al(C₂H₅)₄] with a bath temperature of 80 to 100°C and loaded anodically for a short time to detach the impure surface film. Thereafter, while still moist with electrolyte, the article is lowered under inert gas (N₂) directly into an aluminising bath and aluminium is electrodeposited thereon cathodically with electrode movement.

Besides these surface pretreatment processes, it is possible to use other processes carried out under anhydrous aprotic liquids to obtain bright surfaces free from a covering layer which make it possible to provide a bright surfaced article for immersion in the aluminising bath without coming into contact with moisture. It is thus possible to obtain a similar effect when structural parts are freshly made from solid material by machines under oil, which parts, after perchloroethylene degreasing and toluene

washing, can be introduced directly into the aluminising bath, while covered with toluene so that at no time will surfaces to be aluminised not have been covered with an anhydrous aprotic liquid.

The electrodeposition of aluminium can be effected using an aprotic organoaluminium electrolyte medium which is free from oxygen and water. The electrolyte advantageously contains alkyl aluminium. By using selected current and electrolysis conditions, more especially impulse current with polarity reversal cycles at a frequency, for example of from 10 to 200 c/s, the form of deposition of the electro-deposited aluminium can be influenced in advantageous manner. The particular form of the crystallinity of the coating obtained produces a matt, dazzle-free surface. Normally, the deposition level is from 1 to 2 amp/dm². However, good depositions can still be obtained at up to 6 amp/dm². With a higher current intensity, continuous movement of the cathode or of the electrolyte should be preferably carried out to allow dissipation of current heat being produced.

In principle, all organoaluminium electrolytes which correspond to the following general formula are suitable for use in carrying out the process according to the invention:



in which M can be Na⁺, K⁺, Rb⁺, Cs⁺ or a quaternary onium ion with N, P, As or Sb as central atom, or a tertiary onium ion with S, Se or Te as central atom; X is a monovalent anion preferably F⁻ or Cl⁻, but which can also be Br⁻ and I⁻, CN⁻, or N₃⁻ or a monovalent fraction of a polyvalent anion, preferably 1/2 SO₄²⁻; n is at least 1, advantageously 2 or 3, and R is always an organic radical, advantageously an alkyl radical, more especially an ethyl or methyl radical;

R' can be the same as R, but can also be a hydride (H⁻) ion or a halide (F⁻, Cl⁻, CN⁻, N₃⁻);

R'' has the same general meaning as R' and can be the same or different in meaning as or be different from R', and

m indicates the number of mols. of solvent, if any, used to dilute the electrolyte, the solvent when present preferably being used in amount up to pentamolal with respect to each mode of organoaluminium electrolyte.

Suitable solvents for the electrolytic bath are, for example, aromatic hydrocarbons, more especially toluene and xylene, and ethers, advantageously ethers of relatively high boiling point, such as tetrahydrofuran, dipropylether, dibutylether and dioxanes. Electrolyte solutions of this nature are described, for example, in German Patent Specifications Nos. 1,200,817 and 1,236,208. The organoaluminium electrolytes can be used by themselves or in admixture. The conductivities of the electrolytes will

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be raised if they are diluted with aromatic hydrocarbons, for example toluene.

The upper limit of the bath temperature during the aluminising is determined by the thermal stability of the organoaluminium electrolyte and by the boiling point of any solvent which is used. This upper limit is generally above 130°C. A firmly adhering coating of highly pure aluminium is obtained on the metal substrate coated in the absence of oxygen, moisture and corrosive media, so that undesirable intermediate coatings are not obtained. This aluminium coating is very pure and thus silver-bright, extremely ductile and inert to corrosion. The thickness is generally from 10 to 30 µm. Because of its high degree of purity of at least 99.99% of aluminium, irrespective of the nature of the base material of the shaped metal articles, the aluminium coating always possesses high resistance to corrosion and a silver-bright, very decorative appearance. This surface improvement is of considerable commercial value. This applies to the same degree for Be, Mg, Zn, Ti and Al shaped articles.

Furthermore, the aluminium coatings possess very good electrical surface conductivity, because of their ductility (20 kp/mm² HV=200 Newton/mm² HV) (HV=high vacuum), an excellent capacity for being welded by ultrasonics and, after burnishing or polishing, a high reflective power. The high ductility of the aluminium provides structural components of high strength, hard materials, in particular of beryllium, magnesium and titanium alloys, a surface capable of sliding and a metallic sealing under substantial bearing pressures. In addition, they possess excellent capacity for being anodised. This means that further surface modifications to the shaped metal articles coated with aluminium become possible. In addition to the protective effect against corrosion afforded by the silver-bright, but relatively soft aluminium coating, further protective action against corrosion can be achieved with the glass-clear, transparent aluminium oxide layer obtainable by anodisation which, with a hardness value higher than 4000 N/mm² HV, is surprisingly hard and resistant to abrasion so that it protects the surface of the metal article from mechanical damage. The high purity of the electrodeposited aluminium is responsible for the production of these protective layers. The oxide layers can be produced in practically any layer thicknesses in conventional anodising baths. The properties of the oxide layer can be summarised as: glass-clear transparency, high homogeneity and hardness, good insulative power and heat conductivity, colour-true colouring capacity especially when produced in d.c. sulphuric acid baths and very good consolidation behaviour whether produced in d.c. sulphuric acid or d.c. oxalic acid baths or other organic acid baths.

The particular properties of the aluminium, which determine the general commercial uses of aluminium can thus be transferred to the surfaces of other metal materials. For example, the colouring capacity of the coatings which can be produced by anodising, for example in a d.c. sulphuric acid bath and which are characteristic only of aluminium can be imparted to the other metals and to aluminium alloys which are grey or black after anodic oxidation treatment. The surface oxide layers of the Be, Mg, Zn and Ti materials cannot themselves be coloured in this way.

One particular advantage of the process of the invention is that metal and alloy articles, more especially beryllium and magnesium and high-alloyed aluminium articles, which are particularly suitable, because of their high strength and good capacity, for machining or because of their suitability for working in the chill mould, extrusion or pressure casting methods, can be given the excellent surface properties of highly pure aluminium. By providing a coating by the process of the invention, a permanent protection against corrosion is obtained. In fact, for the first time it becomes possible to use some of these materials commercially for certain purposes. For example, it has not so far been possible for magnesium and magnesium alloys to be aluminised.

The electrodeposition of aluminium is effected in the complete absence of hydrogen. This is an important factor with the light metal shaped articles under consideration, especially when they are formed of titanium. If these materials were to take up in their metal lattice any nascent hydrogen, it would have a deleterious effect on their mechanical properties. Hydrogen brittleness and stress corrosion induced thereby cannot occur with materials aluminised by electrodeposition; this is an exceptionally important advantage of the process of the invention. When metal deposition is effected using aqueous electrodeposition baths, some hydrogen is nearly always generated. This has the further disadvantage of reducing the cathode current output. The aluminium deposition is effected free from H₂ deposition in accordance with the process of the invention and is accompanied by cathode current efficiencies close to 100% of the theoretical.

With regard to the aforementioned anodic oxidation aftertreatment, a dense and complete oxide layer can be achieved using conventional techniques on the electrodeposited aluminium coatings in, for example, d.c. sulphuric acid baths. The oxide coatings obtained can be subsequently coloured for example by dyeing or printing and consolidated.

If colouring is not carried out, sealing of the oxide layer can be effected with water at at least 95°C or with superheated steam.

The glass-clear oxide coatings obtained by

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the process of the invention are characterised by extraordinary hardness (400 kp/mm² HV=4000 Newton/mm HV) and resistance to abrasion. They can be coloured with clear colours and can be printed. Furthermore, they have good thermal conductivity with high insulation power and provide a strong protection against corrosion. The oxide coatings can be readily polished mechanically.

- 5 In many cases, where a protection against corrosion is desired, without perhaps the need for a decorative surface appearance, chemical oxidation of the aluminised surface can be effected. In fact, yellowish or greenish protective coatings can be produced on the electro-deposited aluminium if, as a chemical oxidation processes, there is carried out a chromating process of the type used in industry. In other cases, for example, with titanium and titanium alloys, a particularly hard titanium aluminide coating can be produced by causing diffusion to take place between the aluminium coating and a titanium substrate.
- 10 The process according to the invention can be used for coating and for surface modifying different shaped elements formed from base materials having an affinity for oxygen. A surface protection having a pleasing appearance is obtained. This is of particular advantage for components in the dental art, in electronics, the automobile industry and also in air and space travel. Because of its high ductility, the aluminium coating can also be used as a lubricating film. In addition, it is possible to employ such mechanical techniques as buffing and drum-polishing, to produce a surface lustre.
- 15 The lustrous surfaces can be protected by subsequent anodic oxidation from mechanical damage. Another advantage of the high ductility of the aluminium coatings is that they are suitable for use in ultrasonic welding techniques. The surfaces of handle parts, front plates, substrates and pressure-cast components can be improved by anodic oxidation of the aluminium coatings. The oxide coatings provide an excellent bonding base for application of lacquers, synthetic plastic coatings, adhesions and impregnations.

- 20 This invention will now be illustrated by the following non-limiting Examples.
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Example 1 Electrodeposition of aluminium on beryllium discs

Beryllium discs with a diameter of 40 mm. and a thickness of 2 mm. were connected by means of small dovetail pins extending over the marginal edge of the discs so as to hold the discs in contact and fixed in a cathode frame consisting of titanium. After degreasing by passage thereover of perchloroethylene and drying, the arrangement made moist with toluene, was immersed in an aluminising electrolyte consisting of trimethyl benzyl ammonium hexaethyl monochlorodialanate (0.2

molar excess of triethyl aluminium) in toluene (1:3) and was anodically loaded for 15 minutes at 80°C. with intensive stirring of the electrolyte medium. The polarity was then reversed and, with a current strength of 1.1 A/dm² and with further movement of the electrolyte, an electrolytically deposited aluminium coating with a thickness of about 15 µm was deposited in 90 minutes. After removal of the discs from the aluminising cell, any adhering electrolyte was washed off with toluene and the discs were briefly dipped in TRINORM "Al" and washed in water, and then dried with acetone. The discs were observed to have been provided with a fine crystalline, bright electrodeposited aluminium coating.

The beryllium material was firmly coated with the aluminium. The aluminium coating could be anodised or subjected to other surface modifications, for example dyeing, marking, printing, providing inscriptions or sticking.

Example 2

Electrodeposition of aluminium on beryllium parallelepipedic blocks followed by anodisation and dyeing

Four blocks (6×6×16 mm.) consisting of beryllium were fixed in the titanium cathode frame used in Example 1 by means of two titanium pointed contacts fitting over the square end surfaces, and surface-treated by pressure blasting in oil (1:1 mixture of paraffin oil and silicone oil) with fine electrocorundum of 70 µm under a blasting pressure of 6 atm gauge. Immediately thereafter, the blocks were washed in a perchloroethylene dipping bath, degreased in a perchloroethylene vapour bath and rinsed in toluene. While still moist with toluene, the clamped beryllium blocks were lowered under an atmosphere of dry N₂ gas into an aluminising cell, which was charged with the electrolyte of constitution



with the temperature of the electrolyte bath kept at 95—100°C. and with mechanical movement of the cathode, electrodeposition of aluminium was carried out with a current strength of about 1.0 A/dm² over a period of three hours, with a polarity reversal cycle of 4:1, when an aluminium coating having a thickness of about 30 µm was deposited with strong adhesion and homogeneously on the surface of the beryllium blocks. Any adhering electrolyte was removed by washing the blocks in toluene, blowing until dry and briefly dipping in TRINORM "Al".

Immediately thereafter, with the beryllium parts still retained in the titanium frame, anodisation was effected in a direct current sulphuric acid bath at a temperature of 18°C. In 35 minutes, a colourless, transparent aluminium oxide layer was formed to a thickness of about 12 µm.

- Before effecting the consolidation or sealing of the oxide layer by immersion in boiling deionised water for about 30 minutes, one coated beryllium block was dyed in a dye bath containing 5 g/litre of aluminium pure red B3LW (marketed in Germany by SANDOZ AG/Basle) for 10 minutes at room temperature. In contrast to the red dyed block obtained, uncoated beryllium blocks possessed a lead-grey surface colour tone, and undyed blocks covered with the oxide of electrolytically deposited aluminium had a matt silver-bright colour tone.
- Shaped elements formed from beryllium alloys, more especially high-percentage beryllium-aluminium alloys with 48 to 52% beryllium content, can also be coated and dyed, printed or inscribed in the same way as shaped elements formed from pure aluminium. Suitable dyestuffs for the purpose include the Aluprint dyestuffs marketed in Germany by SANDOZ AG/Basle.
- Example 3**
- Electrolytic deposition of aluminium on cylindrical members consisting of magnesium alloy
- Two cylindrical members with a diameter of 70 mm. and a height of 100 mm. and made of magnesium alloy were mounted on rotary supports consisting of titanium rods and their surfaces were subjected to a surface pretreatment by pressure blasting using 80 μm glass blasting beads with a blasting pressure of 6 atm gauge while immersed in perchloroethylene. After rinsing the members with hot perchloroethylene followed by passage therewith of perchloroethylene vapour, the still hot members, together with the rotary holder, were immediately lowered into an aluminising bath containing
- $$\text{Na}[(\text{CH}_3)_3\text{AlFAI}(\text{C}_2\text{H}_5)_3] \cdot 2.5\text{C}_6\text{H}_5\text{CH}_3$$
- at a temperature of 100°C. and aluminised between two aluminium anode plates (spacing 15 cm) with a cathode movement of 10 cm/sec. and rotation of the parts. Serving as current source was an impulse generator which, with a cathodic/anodic polarity reversal cycle of 4:1 (rectified value of the cathode current 12 amps and of the anode current 3 amps) and 50 c/s deposition frequency under about ± 5 V deposition voltage (amplitude height), permitted an average current strength of about 1.5 A/dm² to be applied to the objects to be aluminised. After a deposition time of two hours, a silver-bright, pore-free and firmly adhering electrodeposited aluminium coating was found to have been obtained in a thickness of about 30 μm on the wall surface. The cathode frame supporting the aluminised magnesium cylinders was raised into a dry N₂ gas atmosphere from the aluminising bath and was sprayed with toluene and thus cleansed from adhering electrolyte.
- It was found in similar experiments that other shaped magnesium articles can be provided with an aluminium coating. Since magnesium articles are frequently used commercially, because of their deformability, in commercial casting procedures, the number of applications of magnesium articles is still further increased.
- Example 4**
- Electrolytic deposition of aluminium, followed by anodisation and dyeing, of bars consisting of Elektron metal, containing 90% and more of magnesium and additions of aluminium, zinc, manganese, copper and silicon.
- 8 Elektron bars (Elektron is a Registered Trade Mark) having the dimensions 135 \times 26 \times 16 mm., and provided with longitudinal grooves of a width of about 1 mm. and a depth of 0.5 mm., were fixed in two rows in a titanium cathode frame measuring 300 \times 500 mm. by means of titanium point contacts over the main, as against end, surfaces of the bars. After intensive perchloroethylene vapour degreasing and rinsing in a toluene-filled ultrasonic bath, the toluene-moist components were introduced under a N₂ protective gas into a melt electrolyte bath at a temperature of 90—100°C. and consisting of 50% by weight Na[Al(C₂H₅)₃] and 50% by weight K[Al(C₂H₅)₄]. The electrolyte was continuously stirred and the titanium frame with the electron bars was anodically loaded for 15 minutes with a current intensity of 1.8 A/dm² and a thin 2 μm magnesium surface film was detached, together with the oxidic surface layer. A nickel grid served as cathode. This pretreatment bath was arranged in close proximity, for convenience of operation, to an 80 litre aluminising bath and the titanium frame moist with electrolyte was directly transferred under the N₂ protective gas from the pretreatment bath into the aluminising cell. If such direct transfer had not been possible, the titanium frame with the now metallically bright electron components would have had to have been rinsed with toluene and the toluene-moist components would then have been introduced into the aluminising bath.
- $$\text{Na}[(\text{C}_2\text{H}_5)_3\text{AlFAI}(\text{C}_2\text{H}_5)_3] \cdot 4.0\text{C}_6\text{H}_5\text{CH}_3$$
- at 80°C. was used as the electrolyte in the aluminising cell. Employing a cathode movement of 6 cm/sec. and a current strength of 1.2 A/dm², the bars were provided by means of impulse current (5:1) and 25 c/s in 2½ hours with an electrodeposition of aluminium coating in a thickness of about 25 μm . After spraying with toluene, rinsing with hot water and dipping for a few seconds in TRINORM "Al", the aluminised electron bars were electrolytically oxidised in a direct current bath for 20 minutes at 18°C. The completely trans-

- parent oxide coating produced, in a thickness of about 8 μm , was dyed a golden colour in 5 minutes, using a dye bath of Al-Pure Gold-L (marketed in Germany by SANDOZ A.G.) (2 g/l), at a temperature of 60°C. The dye was sealed in by immersing the Elektron bars in boiling water for 30 minutes.
- Example 5**
- Electrolytic deposition of zinc pressure-cast articles, followed by anodisation, printing and dyeing.
- Toy cars (about 60×28×20 mm.) made from zinc pressure-cast alloy, DGZnAl4 or
- $$[(\text{CH}_3)_4\text{N}] [(\text{C}_2\text{H}_5)_3\text{AlClAl}(\text{C}_2\text{H}_5)_3] \cdot 0.2 \text{ Al}(\text{C}_2\text{H}_5)_3 \cdot 3.2 \text{ C}_6\text{H}_5\text{CH}_3$$
- Employing a cathode movement of 10 cm/sec. and using the current conditions indicated in Example 3, the zinc pressure-cast toy cars were provided on their external surfaces with an electro-aluminium coating in a thickness of about 30 μm .
- Half of the aluminised zinc pressure-cast toy cars were polished by drum-polishing using steel balls having a diameter of 2 mm. in a rotating polyethylene drum and were then electrolytically oxidised in a direct current bath at 15°C., while the other half were electrolytically oxidised without polishing.
- Before the electrolytic oxidation, the internal surfaces of the toy cars were covered with a covering lacquer which was resistant to sulphuric acid. The external surface was then electrolytically coated with an oxide layer in a thickness of 15—20 μm . from a d.c. sulphuric acid bath. After thorough washing of the oxide surfaces, these surfaces were then printed by means of Aluprint "black" colour paste (marketed in Germany by SANDOZ AG/Basle) with markings and inscriptions and thereafter dyed in a dye bath of Al-Blue-LLW (marketed in Germany by SANDOZ A.G.) (3.5 g/l) at room temperature for 5 minutes.
- Sealing or consolidation of the dye was then effected by immersing the dyed cars for 30 minutes in boiling water of pH 5.5.
- In this manner, it was possible to produce both lustrous and non-dazzling, matt, abrasion-resistant, printed and dyed aluminium oxide surface coatings.
- Example 6**
- Electrolytic aluminising followed by anodisation of hollow cylinders formed from a malleable aluminium alloy.
- 5 columns, each formed from 8 hollow cylinders (20 mm. external diameter, 54 mm. length, 1.5 mm. thickness) consisting of AlZnCu 1.5 F53 were fixed one upon the other while being contacted with threaded parts consisting of titanium belonging to a titanium frame designed to fit an 80-litre illuminising cell. The parts were surface-treated in a pres-
- DGZnAl4Cu1 being used in different runs, were each clamped with a mutual spacing of 20 mm. lengthwise in a titanium frame by means of two pointed clips of titanium, and surface-treated by pressure-blasting with electrocorundum (70 μm) in thinly liquid paraffin oil at a blasting pressure of 5 atm. gauge. After washing in perchloroethylene and degreasing in perchloroethylene vapour, rinsing was carried out in toluene. The titanium frame, still moist with toluene, was transferred with the toy cars under a N₂ atmosphere into an aluminising electrolyte in this case
- sure-blasting apparatus. For this purpose, the columns were rotated while being impacted with a jet of 120 μm corundum powder suspended in paraffin and silicone oils under a blasting pressure of 6 atm gauge. The cylinders had been freshly manufactured, and had been supplied coated with oil. They had been immediately clamped in position. Because they had not been subjected to much atmospheric oxidation, only a surface layer of μm thinness had to be removed.
- After washing with perchloroethylene, degreasing with perchloroethylene vapour and rinsing in toluene with ultrasonic action (about 6 minutes altogether), the clamped, toluene-moist cylinders were transferred by way of an inert gas lock chamber into the 80-litre aluminising cell containing
- $$\text{K}[(\text{C}_2\text{H}_5)_3\text{AlFAAl}(\text{C}_2\text{H}_5)_3] \cdot 4.2 \text{ C}_6\text{H}_5\text{CH}_3$$
- Employing a cathode movement of 13 cm/sec. and using an impulse current having the average current strength of 1.2 A/dm² and a polarity reversal cycle of 4:1 with 50 c/s, the cylinders were aluminised for 1½ hours. The thickness of the electrodeposited aluminium coating obtained in that time was about 15 μm . The coating had a fine-grain silver-bright appearance.
- After washing with toluene, dipping in TRINORM "Al" and rinsing with water, the cylinders were anodised in a direct current bath at 18°C. for 20 minutes (17.5 V, 1.5 A/dm²). A transparent aluminium oxide layer of about 6 μm was obtained. The cylinders were sealed for 20 minutes in superheated steam at 110°C.
- Ultra-pure aluminium and refined aluminium, the purest types of aluminium which are available industrially, are generally too soft and have too little mechanical strength for most commercial constructional uses. In tests for machining them mechanically by drilling, milling, grinding, etc., they "flow" and become distorted. Their practical uses are substantially limited to pressing, stamping and

rolling. In contrast, aluminium alloys, for example Al-Mg, Al-Cu, Al-Si and Al-Zn alloys possess high strength, good mechanical machining properties and deformability allowing their being worked by hot-pressing, forging and casting, so that these alloys have acquired exceptionally great importance in vehicle, ship and aircraft construction and practically all other technical fields. The alloy partners and impurities, more especially Si, Mn, Cu, Fe and Pb, have hitherto had a deleterious effect on the anodisation of aluminium workpieces, for example, because of the resulting reduced hardness or natural colour of the alloys. Using the process according to the invention, a highly pure electrolytically deposited aluminium layer having commercially valuable properties can be applied to these materials. The range of use of the aluminium alloy is thus substantially increased.

Example 7

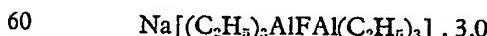
Electrolytic aluminising of aluminium pressure-cast perforated plates

Three perforated plates of dimensions $110 \times 60 \times 3$ mm. and formed from DG Al Si12 were attached by titanium point contacts fixed over their narrow sides to a titanium frame and surface-treated by pressure-blasting with a corundum (SN120)-oil suspension under a blasting pressure of 5 atm gauge. Washing and degreasing were carried out as in Example 6. The toluene-moist parts were then aluminised for 3 hours at 100°C . in an aluminising bath consisting of triethylphenyl ammonium chloride and 2.2 triethyl aluminium, dissolved in the same volume of toluene. A cathode movement of 15 cm/sec. was employed together with aluminium anodes spaced apart at 5 cm. intervals. A current strength of $1.0 \text{ A}/\text{dm}^2$ was used.

Example 8

Electrolytic aluminising followed by partial anodisation and dyeing of aluminium sheets.

Six sheets having the dimensions $100 \times 50 \times 2$ mm. and consisting of pure aluminium, 99.5% Al, arranged in two rows one above the other and contacted by titanium pointed contacts were fixed in an insulated titanium frame with which contact was simultaneously made. The surfaces of the sheets were degreased by etching with dilute caustic soda solution and cleaned. After being vigorously rinsed in water, the water was removed by dipping in acetone and then toluene and the titanium frame with the sheets was then dipped under N_2 gas into an electrolyte consisting of



toluene.

To remove the oxidic-hydroxidic surface

layer, which is formed by the aluminium coming into contact with water, the sheets were anodically loaded for 10 minutes at $3 \text{ A}/\text{dm}^2$, with reciprocatory movement of the titanium frame (15 cm/sec.) and mechanical circulation of the electrolyte, which was at 90°C . This resulted in the surface layer being detached together with a thin aluminium film.

Immediately hereafter, the now metallically bright surfaces were coated in a firmly adhering manner with an electrolytically deposited aluminium layer in a thickness of about 20 μm in the same electrolyte, by polarity reversal with $2 \text{ A}/\text{dm}^2$ average current strength and the usual impulse current conditions (see Example 6). Electrodeposition was continued for 55 minutes. After washing with toluene, dipping in TRINORM "Al" and rinsing in water, drying of the sheets was carried out with acetone.

For partial electrolytic oxidation of the sheets, the rectangular surfaces of the aluminised sheets were covered with a self-adhering, acid-resistant synthetic plastic foil, which was cut in the form of a meander pattern with webs 5 mm. wide. Anodising was now effected for 30 minutes in a direct current oxalic acid bath at a temperature of 15°C . and an oxide layer about $12-15 \mu\text{m}$ thick was produced on the surface portions and edges which had remained uncovered. After intensive rinsing in water, the adhesive foil was detached, washing was again carried out and the oxide layer was dyed for about 5 minutes in a dyebath of Al-Black-MLW (marketed in Germany by SANDOZ A.G.) (10 g/l) at 60°C . Finally, the oxide layers, which had been dyed black, were sealed in boiling water for 30 minutes.

Since aluminium oxide layers are not attacked when the meander sheets are anodically loaded in the aluminising electrolyte, although a surface film of electrodeposited aluminium can however be detached, the surface treatment of the sheets in the electrolyte as initially described could be repeated after removal of the adhesive foil and then, by polarity reversal, the meander surface could be thickened or strengthened with electrodeposited aluminium up to the level of the oxide surface.

Example 9

Electrodeposition of aluminium on titanium sheet strip followed by surface improvement by aluminium diffusion

Titanium sheet strip (samples of the "CONTIMET" (Trade Mark) 30 or 35 type being used in different tests) with a width of 160 mm. and a thickness of 0.5 mm., were subjected to a continuous surface pretreatment followed by two-sided aluminising in a continuously operating strip-aluminising plant.

The surface pretreatment of the titanium strip was carried out by pressure-blasting with fine silicon carbide particles of $100 \mu\text{m}$ sus-

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pended in an aprotic solvent, trichlorotrifluoroethane ("FRIGEN" (Trade Mark) 113), although carbon fluorides boiling at higher temperatures could conveniently have been used. A blasting pressure of 10 atm gauge was used, the SiC particle suspended being supplied from blasting nozzles arranged on both sides of the strip. Pressure blasting was carried out under a nitrogen atmosphere. In other tests, liquid drop bombardment erosion with

FRIGEN 113 (specific gravity 1.58 g/ml) or with a liquid carbon perfluoride of even higher specific gravity was effected. In the former case, the strip, after the surface pretreatment with FRIGEN 113, was washed free from particles and dried under N₂ gas. The bright titanium strip free from a surface layer was then passed through into the aluminising cell and coated therein on both sides with about 10 µm aluminium electrodeposited from



A maximum current strength of 6 A/dm² was employed during a passage time of 10 minutes. In order to make this relatively high rate of deposition possible, the cathode-anode spacings were reduced to 10 mm. and the electrolyte liquid was rapidly circulated by pumping in counter-current between the sheet strip cathode and the two aluminium anodes.

The coated Ti sheet strip was rinsed with toluene and dried and loosely wound. After being kept in this state for 2 hours at 600°C., the aluminium was found to have diffused into the titanium to a depth of 5—10 µm.

The surface pretreatment, aluminising and diffusion were carried out in the complete absence of hydrogen.

Titanium alloys, which are becoming of ever-increasing importance in the construction of turbines and engines, in the rocket and nuclear reactor arts and also in aircraft construction, can be surface-modified in similar manner. Aluminium is the alloy partner present in the largest quantity, in the titanium alloys which are of greatest commercial importance, for example,

Ti Al Mo 8-1-1	7.5 —8.5%	Al
Ti Al Mo 74	6.5 —7.3%	Al
Ti Al 64	5.75—6.75%	Al
Ti Al Sn Zr Mo 6-2-4-2	5.5 —6.5%	Al

This is because aluminium improves the strength of the titanium. By carrying out the process of the invention, unalloyed titanium which usually can still be satisfactorily deformed, can be electrolytically coated with aluminium. As a result of aluminium being diffused into the surface of the workpiece, particularly hard Ti-Al alloys can be produced. Titanium sheets used for the construction of containers and in connection with aircraft skins can thus be provided with a harder surface which possesses better heat resistance and better resistance to abrasion than pure titanium. Electrolytically deposited aluminium layers on titanium workpiece surfaces, which layers may have been anodically oxidised, protect the titanium against corrosion, more especially against salt water, and make it possible to produce a commercially and decoratively attrac-

tive surface modification to the steel-hard light metal.

Example 10 Electrolytic aluminising followed by anodisation and dyeing of clutch journals consisting of a titanium alloy

Cylindrical clutch journals having a longitudinal bore with a diameter of 7 mm. and made of TiAlV64 were arranged in 4 columns, each built up from 8 components, in the afore-described titanium rotary frame for an aluminising cell and were surface-pretreated by pressure-blasting with silicon carbide (100 µm) in "FRIGEN" 113, employing a blasting pressure of 8 atm. gauge.

After washing with perchloroethylene and rinsing with toluene, the components were transferred to the aluminising bath and were provided with an electrodeposited aluminium coating in a thickness of about 15 µm. During electrodeposition reciprocal movement of the titanium frame and rotation of the columns were effected.

The columns were then electrolytically oxidised in a direct-current bath to a thickness of about 7 µm and dyed in an Al-Blue-LLW dyebath (dye marketed in Germany by SANDOZ A.G.) (2 g/l) at room temperature for 2½ minutes. The aluminium oxide surface layer, consolidated or sealed for 30 minutes in boiling water, had a homogeneous, light-blue and non-dazzling appearance.

This is particularly important, if a uniform, decorative surface appearance is required with a combination part made of aluminium alloy, brass and titanium material.

WHAT WE CLAIM IS:—

1. A process for applying an aluminium coating to a shaped article formed from a metal which is attacked by aqueous or protic media or by oxygen to form an oxidic or hydroxidic or salt surface coating, which comprises providing the shaped article with surface(s) free from a said coating in the presence of an anhydrous aprotic liquid which is inert to the metal and which covers the surface(s) of the shaped article to be aluminised, and, without exposing said surface(s) to an aqueous or protic

- medium or to oxygen, electrolytically depositing aluminium on the said surface(s) from an oxygen-free and water-free aprotic organo-aluminium electrolyte.
- 5 2. A process as claimed in Claim 1, in which the shaped article is formed from a metal selected from beryllium, magnesium, zinc, aluminium and titanium, and alloys of a said metal which constitutes, or a number of said metals, which, taken together constitute, the major component of the alloy.
- 10 3. A process as claimed in Claim 1 or 2, in which said surface(s) are provided by pretreating the shaped article in the presence of a said aprotic liquid to remove a said coating therefrom.
- 15 4. A process as claimed in Claim 3, in which the pretreatment is effected by pressure blasting said surface(s) with particles of hard material suspended in a said anhydrous aprotic liquid which is insufficiently volatile to vapourise under the pressure blasting conditions used and expose to the ambient atmosphere, said surface(s).
- 20 5. A process as claimed in Claim 4, in which the anhydrous aprotic liquid is an oil.
- 25 6. A process as claimed in Claim 5, in which the oil is selected from paraffin oils and silicon oils.
- 30 7. A process as claimed in Claim 4, in which the anhydrous aprotic liquid is an optionally halogenated hydrocarbon.
- 35 8. A process as claimed in Claim 7, in which the halogenated hydrocarbon is a carbon perhalide.
- 40 9. A process as claimed in Claim 7 or 8, in which the halogenated hydrocarbon is a chlorinated hydrocarbon.
- 45 10. A process as claimed in any one of Claims 4 to 9, in which the hard material is corundum powder.
- 50 11. A process as claimed in any one of Claims 4 to 10, in which the blasting is effected using a blasting pressure of from 1 to 10 atm. gauge.
- 55 12. A process as claimed in Claim 11, in which the blasting is effected using a blasting pressure of from 3 to 7 atm. gauge.
- 60 13. A process as claimed in any one of Claims 4 to 12, in which the hard substance has a particle size of from 50 to 200 μm .
- 65 14. A process as claimed in any one of Claims 4 to 13, in which the pressure blasted surface(s) is/are contacted with liquid perchloroethylene followed by perchloroethylene vapour before being aluminised.
- 70 15. A process as claimed in Claim 14, in which the perchloroethylene contacted surface(s) bearing a coating of condensed perchloroethylene is/are immersed in toluene before being aluminised.
- 75 16. A process as claimed in Claim 3, in which the pretreatment is effected by liquid drop bombardment erosion of said surface(s) with a said anhydrous aprotic liquid.
17. A process as claimed in Claim 11, in which the shaped article is in strip or sheet form.
18. A process as claimed in Claim 16 or 17, in which the anhydrous aprotic liquid comprises benzene or toluene.
19. A process as claimed in any one of Claims 16 to 18, in which the pretreatment is carried out under a nitrogen atmosphere.
20. A process as claimed in Claim 16 or 17, in which the anhydrous aprotic liquid is a carbon perhalide.
- 25 21. A process as claimed in Claim 3, in which the pretreatment is effected by anodic detachment of a thin surface layer of the said article in an oxygen-free and water-free aprotic organo-metallic electrolyte.
- 30 22. A process as claimed in Claim 21, in which the electrolyte is an organoaluminium electrolyte.
- 35 23. A process as claimed in Claim 22, in which the electrolyte is a tetraalkyl alanate complex.
- 40 24. A process as claimed in Claim 23, in which the complex is the sodium-potassium mixed salt of tetraethyl alanate.
- 45 25. A process as claimed in Claim 22, 23 or 24, in which the electrolyte contains triethyl aluminium and trimethyl aluminium.
- 50 26. A process as claimed in any one of Claims 22 to 25, in which the shaped article is formed from beryllium or aluminium, and the anodic loading is effected in the same cell as that used for the aluminising, and aluminising is effected by reversal of the polarity of the cell.
- 55 27. A process as claimed in any of the preceding claims, in which the aluminising is effected in an electrolyte containing alkyl aluminium.
- 60 28. A process as claimed in Claim 27, in which the organoaluminium electrolyte possesses the following general formula:
- MX . nAIR'R''R + m solvent
- in which M is Na^+ , K^+ , Rb^+ , Cs^+ , a quaternary onium ion with N, P, As or Sb as central atom or a tertiary onium ion with S, Se or Te as central atom; X is a monovalent anion or monovalent fraction of a polyvalent anion; n is at least 1; R is an organic radical; R' and R'' can be the same or different and have the same general meaning as R, or can be hydride or halide radicals; and m indicates the number of moles of a solvent which is optionally present in the electrolyte, with respect to each mole of organoaluminium electrolyte.
- 110 29. A process as claimed in Claim 28, in which the electrolyte contains a solvent in an amount up to pentamolar with respect to each mole of organoaluminium electrolyte.
- 115 30. A process as claimed in Claim 28 or 29, in which the solvent is an aromatic hydrocarbon or an ether.

31. A process as claimed in Claim 30, in which the solvent is selected from toluene, xylene, tetrahydrofuran, dipropyl ether, dibutyl ether and dioxanes.
- 5 32. A process as claimed in any one of Claims 28 to 31, in which X is selected from F⁻, Cl⁻, Br⁻, I⁻, CN⁻, N₃⁻ and SO_4^{2-} .
- 10 33. A process as claimed in any one of the preceding claims, in which aluminising is effected until an aluminium layer having a thickness of from 10 to 30 μm is obtained.
- 15 34. A process as claimed in any one of the preceding claims, in which aluminising is effected using an impulse current with polarity reversal cycles.
- 20 35. A process as claimed in Claim 34, in which the frequency of the polarity reversal cycles is from 10 to 200 c/s.
- 25 36. A process as claimed in Claim 1 for applying an aluminium coating to a shaped article, substantially as described in any one of the foregoing Examples.
- 30 37. A shaped article at least one surface of which has had an aluminium coating applied thereto by the process claimed in any one of the preceding claims.
- 35 38. A process for surface modifying a shaped article as claimed in Claim 37, in which an aluminised surface of the article is anodically oxidised.
- 40 39. A process as claimed in Claim 38, in which said surface of the article is anodically oxidised in a direct current sulphuric acid bath.
- 45 40. A process as claimed in Claim 38 or
- 50 39, in which the oxide layer formed is dyed and/or printed.
- 55 41. A process as claimed in any one of Claims 38 to 40, in which the oxide layer formed is sealed by contacting it with water at a temperature of at least 95°C or superheated steam.
- 60 42. A process for surface modifying a shaped article as claimed in Claim 37, in which an aluminised surface of the article is subjected to chemical oxidation.
- 65 43. A process as claimed in Claim 42, in which chemical oxidation of the aluminised surface is effected by chromating, whereby the aluminised surface is simultaneously coloured.
- 70 44. A process for surface modifying a shaped article as claimed in Claim 37, in which the aluminium coating is caused to diffuse into a surface to which it has been applied.
- 75 45. A process as claimed in Claim 44, in which the shaped article is formed of titanium.
- 80 46. A process for the surface modification of a shaped article as claimed in Claim 37, substantially as described in any one of the foregoing Examples 2, 4, 5, 6, 8 and 9.
- 85 47. A surface-modified shaped article whenever produced by the process claimed in any one of Claims 38 to 46.

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